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Rational design of binder-free $ZnCo_2O_4$ and Fe_2O_3 decorated porous 3D Ni as high-performance electrodes for asymmetric supercapacitor

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ABSTRACT

The development of hierarchical, porous film based current collector has created huge interest in the area of energy storage, sensor, and electrocatalysis due to its higher surface area, good electrical conductivity and increased electrode-electrolyte interface. Here, we report a novel method to prepare a hierarchically ramified nanostructured porous thin film as a current collector by dynamic hydrogen bubble template electro-deposition method. At a first time, we report a porous 3D-Ni decorated with $ZnCo_2O_4$ and Fe_2O_3 by simple, low-cost electrochemical deposition method. The fabricated porous 3D-Ni based electrodes showed an excellent electrochemical property such as high specific capacitance, excellent rate capability, and good cycle stability. The asymmetric solid-state supercapacitor device was fabricated using porous, 3D Ni decorated with $ZnCo_2O_4$ and Fe_2O_3 as the positive and negative electrodes. The fabricated $ZnCo_2O_4$//Fe_2O_3 asymmetric device delivered an areal capacitance of 92 mF cm^{-2} at a current density of 0.5 mA cm^{-2} with a maximum areal power density of 3 W cm^{-2} and areal energy density of 28.8 mWh cm^{-2}. The higher performances of porous, 3D current collector have a huge potential in the development of high performance supercapacitor.

1. Introduction

The rapid growth of human civilization and consumption of the huge amount of energy, as well as deficiency of fossil fuel, makes scientist to rethink the energy conversion and storage research. A lot of efforts have been put into the development and improvement in renewable energy conversion as well as in energy storage devices [1,2]. Recently, a huge attention has been paid to the development of high-performance energy storage devices to meet the world energy crisis. Traditionally, the energy storage devices are classified into two categories such as battery and electrochemical supercapacitors. The supercapacitor is one class of electrochemical energy storage devices. Considerably, a lot of research has been done in the development of high-performance supercapacitor due to their high power densities, longer life cycle, excellent stability, low maintenance, environmentally friendly and fast charge-discharge behavior compared to batteries, even though lower energy densities of these devices obstruct their practical application. Furthermore, a research is still required to develop a high energy supercapacitor without sacrificing their power densities, which is directly related to the specific capacitance of the device [3–6].

The energy storage device is further classified based on their energy storage mechanisms such as electrochemical double layer (EDLC) and pseudocapacitor; the first one stores the charges by forming an electrical double layer at the electroactive and electrolyte interface via an adsorption/desorption and the second one follows the reversible faradic reaction due to the intercalation of electrolyte ions in electroactive materials. The carbon-based materials such as activated carbon, graphene, and carbon nanotube were used for constructing EDLC supercapacitors, which were suffered by lower specific capacitance and rate capability. Compare to EDLC, pseudocapacitor possesses higher theoretical capacitance due to reversible faradic redox reaction during charging and discharging process. Mainly, the transition metal oxides and sulfides, conducting polymer were used for pseudocapacitors but low electrical conductivity of the transition metal oxides reduces the rate capability [6–8].

The specific capacitance of the supercapacitor was improved on different nanostructure electroactive materials such as nanowire, sheets, wall, flakes, particles, and their composites with nanocarbon,

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conducting polymers. Alternatively, a porous 3D current collector was used as a supporting substrate for electrode fabrication, which is an effective and efficient way to improve the specific capacitance of the device in the desired area. Last decades, transition metal oxides and sulfides have been largely explored for this application due to its higher electrochemical redox properties, higher theoretical capacitance and low-cost. However, their poor electrical conductivity reduces its rate capability. Recently, binary transition metal oxides occupy that place because of higher conductivity, rich electrochemical redox reaction sites and multiple oxidation states compare to the corresponding constituent mono metal oxides. Among other binary transition metal oxides, the $ZnCo_2O_4$ material has huge potential as an electrode for supercapacitor application because of low cost, higher electrical conductivity, higher theoretical capacitance, richer electrochemical redox sites, abundant and environmentally friendly. Considerable reports are available in $ZnCo_2O_4$ materials with different nanostructures like nanorods [9], nanowires [10], nanotubes [11], porous microspheres [12], nanosheets [13], and core-shell structures [14–16] at different methods. Until now, there is no report on the synthesis of $ZnCo_2O_4$ through electrochemical deposition method because it is very simple, cost-effective method. Here we report a novel, simple fabrication technique to synthesize the binary metal oxide.

The fabrication of asymmetric supercapacitor is a direct way to improve the specific capacitance of the device by wide operating potential. Until now, most of the asymmetric devices have been fabricated using various carbon materials as a negative electrode, and only few metal oxides such as Fe_2O_3, Fe_3O_4, FeOOH, Bi_2O_3, Bi_2WO_6, MoO_2, MoO_3, WO_3, VN, TiN were studied [17–26]. Compare to positive electrodes, negative electrode showed lower specific capacitance, so further studies were required to develop higher capacitive materials as well as improve the capacitance of the available materials. Among metal oxide materials, α-Fe_2O_3 has been a promising material for negative electrode because of the large potential window, higher redox activity, and low cost. So in this work, we choose α-Fe_2O_3 as a negative electrode to explore the electrochemical performance for fabricating the asymmetric device.

The three dimensional (3D) porous metal skeleton based current collectors are attracted huge attention in the energy storage, sensor, electrocatalysis, and fuel cell, because of the high surface area, micron size pore and ramified metal nanoparticle network on pore walls. Many methods have been adopted to make porous metal electrodes such as lyotropic liquid crystalline phases [27], electrochemical dealloying [28], electro-deposition within the interstitial spaces between colloidal spheres [29,30] and dynamic hydrogen bubble templated electro-deposition [31–33]. Compare to other methods, hydrogen bubble template electro-deposition method has more advantages like stable porous structure, easily controlled pore formation of ramified nanostructured walls. Considerable attention has been paid to the development of various porous 3D metal films with different metals such as Ag, Au, Cu, Ni, Sn, Co, Pt and metal alloys for various applications using this method [31,33–36]. There are only a few reports available in supercapacitor using this 3D structure with various electroactive materials such as $NiCo_2O_4$, $NiCo_2S_4$, Co_2O_3, $Co(OH)_2$, $Ni(OH)_2$, which motivated us to develop a 3D, a porous electrode with new electroactive materials [35,37–39].

In this study, we report a fabrication of porous 3D-Ni skeleton decorated $ZnCo_2O_4$ and α-Fe_2O_3 using a simple, low-cost electrochemical deposition followed by thermal annealing. To the best of our knowledge, this is the first report on the fabrication of $ZnCo_2O_4$ nanostructures with 3D porous structures by electrochemical deposition. Further, we have fabricated asymmetric device using porous 3D Ni decorated $ZnCo_2O_4$ and Fe_2O_3 as the positive and negative electrodes, respectively. The detailed fabrication and electrochemical performance of the electrodes and device are discussed.

2. Experimental section

2.1. Materials

All the chemicals were analytical grade and used without further purification. The following chemicals were used in this work such as zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, Samchun, Korea), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, Junsei, Japan), sodium nitrate (Sigma Aldrich), potassium hydroxide (KOH, Samchun, Korea), nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, Sigma Aldrich), iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, Sigma Aldrich), ammonium chloride (NH_4Cl, Yakuri, Japan), hydrochloric acid (HCl, Samchun, Korea), stainless steel (SS) (SUS304, Nilaco, Japan), nickel foam. All the aqueous solutions were prepared with deionized water (18.2 MΩ cm, Elga DI water system).

2.2. Fabrication of porous three dimensional (3D) Ni network thin film current collector

Three dimensional (3D) Ni skeleton current collector was fabricated in stainless steel by dynamic hydrogen bubble templated electrochemical deposition [31,33,38,40]. First, commercial stainless steel (SS) with the area of 3 cm × 1 cm was cleaned with 5 M HCl and subsequently washed with DI water. The cleaned SS (1 cm^2) was used as a cathode and platinum plate as an anode with separation of ~ 1 cm. The electrochemical deposition was carried out in 2 M NH_4Cl and 0.1 M $NiCl_2$ electrolyte solutions at a high current density of 2.5 A cm^{-2} for 60 s in ambient condition. The prepared 3D-Ni skeleton was repeatedly cleaned with water and ethanol and dried in a vacuum oven for 12 h.

2.3. Preparation of $ZnCo_2O_4$ nanoflakes-decorated porous 3D-Ni (3D Ni-$ZnCo_2O_4$) current collector for the positive electrode

The $ZnCo_2O_4$ nanoflakes were coated over 3D-Ni current collector by the electro-deposition method. The electro-deposition was carried out in three-electrode configuration with a potential of −1.2 to 0.2 V at a scan rate of 50 mV s^{-1} for 2 cycles in an electrolyte solution containing 20 mM of zinc nitrate, 40 mM of cobalt nitrate and 100 mM sodium nitrate. Here, 3D-Ni current collector/nickel foam, platinum wire, and Ag/AgCl were used as a working, counter and a reference electrode, respectively. After electro-deposition, the samples were consecutively rinsed with water and ethanol and then dried in a vacuum oven for 12 h. Further, dried samples were annealed at 300 °C for 2 h at a heating rate of 1 °C min^{-1} in ambient air.

2.4. Preparation of Fe_2O_3 nanoleaf-decorated porous 3D-Ni (3D Ni-Fe_2O_3) current collector for the negative electrode

The Fe_2O_3 decorated 3D Ni negative electrode was prepared by a two-step process. First, Fe nanoparticles were deposited over 3D Ni skeleton by cathodic deposition in an electrolyte solution containing 1 M NH_4Cl and 0.05 M $FeCl_3{\cdot}6H_2O$ at a current density of 1 A cm^{-2} for 20 s in ambient condition. The prepared Fe deposited 3D Ni current collector was repeatedly cleaned with water and ethanol and followed by drying in an oven for 12 h. In the second step, as prepared Fe decorated 3D Ni current collector was annealed at 250 °C for 3 h in a hot plate at ambient condition [41].

2.5. Fabrication of asymmetric solid-state supercapacitor device

The solid-state asymmetric supercapacitor device was assembled by using 3D Ni-$ZnCo_2O_4$ and 3D Ni-Fe_2O_3 as positive and negative electrodes with PVA-KOH gel electrolyte. The detailed preparation of PVA-KOH and assembling of the device as described in our previous report [40]. The assembled device was allowed to dry in ambient condition for several hours to remove the excess water in the gel electrolyte. The